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ADHESION BETWEEN ATOMICALLY CLEAN SURFACES

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INTRODUCTION

The purpose of the research on adhesion bonding between metallic solids under this program was to identify the underlying mechanisms and interaction processes involved when two atomically clean metallic surfaces are brought together and form a stable interface. It was anticipated that if these mechanisms could be understood entirely the seizure problem between metals in contact under space conditions could be minimized through knowledgeable materials selection. For example, total seizure should not necessarily be the end result in a mechanical system exposed to ultra high vacuum when the lubricant is expended. to p 1

The progress on the solution of this problem may readily be separated into two distinct regions, i.e. theoretical analysis of the problem and experimental. Although the latter was somewhat limited due to the restrictions imposed on the supplemented grant, a great deal of progress was incurred on the scope and basic nature of adhesion. The analytical progress was a direct outgrowth of the publication presented to the Vacuum Society and the massive amount of correspondence immediately thereafter. The paper was reviewed in Product Engineer, United States; New Scientist, England; and Wear, Netherlands. After a number of discussions with a number of principals in the field of adhesion a request by the editor of Wear was accepted to publish a discussion of the nature of adhesion in a review article. Since this article constitutes a complete analysis of mechanisms of adhesion it is included as the "Analytical Section".

A discussion of the experimental progress was presented to the joint NASA-DOD symposium on "Space Lubrication" May 3, 1963 and is to be published therein.

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ANALYSIS OF ADHESION MECHANISMS *all*

[DIFFUSION BONDING]

Summary

A broad definition of adhesion between solid metals is proposed and discussed in order to permit a better understanding of the vast amount of metallic adhesion data being published currently. An interesting result of the definition in this paper is that there appears to be a real relationship between adhesion phenomena and the processes of friction, cold welding, sintering, grain boundaries strength and fatigue. A number of experimental techniques are discussed and analyzed with respect to increasing our knowledge of adhesion phenomena. *end* *Mull* *3-31-64*

Introduction

During the past few years there has been a renewed and expanded interest on the subject of metal-metal adhesion where the term adhesion has indicated the joining of two metals at room temperature through some chemical or micromechanical mechanism. Although adhesion appears to be closely related to the normal processes of friction, or cold welding, as shown by Bowden and his co-workers (1-3), probably the greatest impetus for these studies is the increased probability of the occurrence of metal-metal adhesion, i.e. increase in the frictional coefficient, as the atmospheric pressure is decreased to conditions simulating those observed in outer space. With the failure of conventional lubricants under such conditions the problem of total seizure of bearings and other moving parts in a space environment, becomes an immediate concern. If the extent of adhesion can be reduced to a minimum value or the mechanism understood to a degree where control is possible, there is little doubt that the other components of the frictional coefficient can be reduced through normal design procedures. If in the minimizing of the adhesion component the true nature of adhesion is also unlocked, we can then expect a better understanding of processes of normal friction, cold welding, sintering, and possibly even grain boundary strength or fatigue.

The scope of adhesion phenomena is apparent from the list of processes just cited; however, a slightly broader view might permit a better conception of the problem to be solved. The microlimiting case might conceivably be the adhesion or adsorption, of one metallic atom, or more realistically, a monolayer of metallic atoms on a metal substrate. This category would probably fall under the study of metallic adsorption, or "sitting time" of a metallic atom on a hot substrate as discussed by Hughes and Levinstein (4, 5). The next category may be the development of the monolayer into a bulk phase many thousands of atoms thick. The metal phase held to an undisturbed substrate by some form of chemical or electrostatic bonding is that which we shall call chemical adhesion. At the macro-end of the scale we should consider the mechanical interlocking of one phase to another in which the interlocks may be only a few hundred atoms

thick; but, of sufficient number to create an apparent interfacial bond strength. In the following paragraphs a few of the more obvious problems involved in the study of chemical adhesion will be considered rather than an exhaustive survey of the extremely broad field.

It is interesting that when Gregg defined surface energy in his recent book (6) he also unintentionally set the conditions for a definition of ideal chemical adhesion. That is, the surface free energy was defined as the reversible isothermal work (2γ) required to pull apart in vacuum a one square centimeter of cubic cross section of pure material of perfect crystal structure. Gregg also cited the modifications necessary to this definition, if a gas were adsorbed on this surface which in turn would create an irreversible process. It should be evident that the irreversible process would have a lower energy of return since the unbalanced surface status created in the breaking process would have been, in part, satisfied through an adsorption reaction. Chemical adhesion may then be considered as one half of the isothermal reversible work required to separate and replace to exact coincidence one square centimeter of interface at a temperature of absolute zero in a perfect vacuum. The processes of extrusion or injection of one phase into, or around, the surface of the second phase, or the mechanical interlocking of surface irregularities constitutes a second adhesion problem which relies more upon the mechanical properties of the original materials rather than the interaction chemistry of the two phases and may be considered as mechanical adhesion. Following this proposal, the ideal energy of adhesion would be defined as the surface energy of that material, or if two different materials were involved, the interfacial energy. This definition assumes that the return of the interface after it has been created, in either case, to be ideal, that is, the atomically planer surfaces must interact without an imposed mechanical force in perfect atomic coincidence at absolute zero. The energies in the ideal case should be related directly to the cohesive energy of the solid with respect to the type of atomic bonds formed. In the case of ideal adhesion between unrelated metal couples, the junction cannot be considered in chemical equilibrium as would be the case in a simple grain boundary in which the electrochemical potentials of the components in each phase are equal.

Although the definition cited above should be quite unattainable by even the most careful experiments, and has little meaning when applied to friction or wear processes, it does allow some insight into the nature of adhesion and permits a degree of analysis of the great quantity of adhesion data being presented in the current literature. With this in mind let us examine each of the various restrictions set by the ideal definition of adhesion and consider each of their contributions.

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Interaction Geometry

The possibility of perfect atomic or planer coincidence during ideal adhesion between surfaces of the same metal is infinitely small without the aid of atomic diffusion. Since the predicted free surface energy of a material varies to some extent from one crystallographic direction to another (7), one would not expect the adhesion energy of a mismatched system to be as high as that of an ideal case. A more interesting influence occurs when the actual atomic bonds across the interface are considered in relation to the degree of misalignment of the atoms and their respective planes. In a review of the nature of solids, Hume-Rothery (8) illustrates that covalent and ionic solids rarely involve more than six atomic bonds per atom and metallic solids may involve as many as 14 bonds per atom, if we consider the next nearest neighbors contribution of the body-centered cubic configuration as significant. A further point to be considered lies in the general nature of the respective types of bonds, that is, a pure covalent bond exhibits rather exact bond lengths and respective bond angles, and this is also true, but to a lesser extent, in ionic solids. Metals, however, exhibit great flexibility particularly in bond angle as demonstrated by the ability of a metal to retain or even improve its strength properties when the system is work hardened or mechanically strained. One might infer from this that unless the adhesion were ideal one would expect a poor degree of bulk adhesion strength from a covalent or ionic interface. The extreme brittleness of polycrystalline silicon, germanium or partially ionic nickel-aluminide may be cited as examples of mismatch across the grain boundaries. This may be further illustrated in the poor ability to form powder compacts of organic materials, silicon, diamond, or ionic salts at temperatures well below their atomic diffusional range. In contrast, high purity, degassed nickel powder will compact under its own weight below 400°C. In confirmation of these observations a series of several unsuccessful attempts (9) to join two pieces of high purity single crystals of germanium at room temperature under nearly ideal conditions were made in an apparatus described in the section "Surface Impurities". These crystals were oriented to coincide within 10° of each other.

The preparation of atomically planer surfaces has met with little success and as a result, even the smoothest of surfaces have discontinuities in the form of steps and holes in the order of 10 - 500 Å. As a consequence, surface to surface contact usually involves localized pressures at contact points, asperities, which are of sufficient magnitude to cause plastic deformation of the respective asperities.

In the cleavage of certain inorganic compounds, atomic coincidence does not appear to be a limiting factor in the execution of the ideal adhesion experiment as discussed in the definition. Coincidence was, in all probability, maintained in the excellent study of the surface energy of mica by Bailey (10) in which

the force necessary to separate layers in a reversible sense was measured very precisely. This force related to the relatively weak potassium-oxygen electrostatic bond strength which allowed interlayer cleavage rather than the rupture of the more covalent bonds lying within the layers. The entire process was permissible since the elastic limit of the layer itself is not exceeded in a partial cleavage, i.e. retention of coincidence. The fracture of a metal, on the other hand, always involves some degree of plastic "relaxation" of the surface; thus, retention of coincidence would be impossible even if a crack could be initiated without the introduction of stresses. Polarization forces mentioned by Weyl (11) in the case of most ionic compounds serve the same cause.

The reduction in adhesion strength due to misorientation in metal couples of the same metal may provide a basis for structure weakening during the process of fatigue. For example, during the fatigue process metal crystallites are shifted about during the first step of deformation and supposedly returned during the second. In the light of the above discussion it is unlikely that the return process, even though fracture did not occur, would place the atoms back to identical coincidence; hence, a loss in strength due to the creation of an interface. If microcracks were formed near the surface, atmospheric gases could rapidly diffuse to the crack apex and further reduce the probability of adhesion during the return deformation process. Since both mechanisms would be involved one would not expect the complete elimination of the adsorption process, i.e. fatigue in ultra high vacuum, to eliminate the strength loss due to fatigue; but, this might afford a method to separate the variables.

In conclusion, it appears that on the basis of geometrical considerations the accurate ideal adhesion energy, or for that matter surface energy data for metallic solids will be very difficult to obtain by the cleavage techniques.

Surface Impurities

The surface of a metal under atmospheric conditions may be considered as existing in at least three layers and involving two or possibly three interfaces. The first interface consists of an equilibrium region between the gaseous atmosphere and the gas atoms adsorbed on the oxide surface (neglecting surface greases). The oxide itself may consist of several layered chemical compounds. The next interface is that between the oxide and the metal substrate. A deformed metal layer may or may not exist as a barrier to the bulk metal phase. In effect we have a sandwich structure consisting of a brittle surface oxide with a relatively ductile substrate of metal. In metal adhesion the primary strength of the macro-bond will probably come from metal-metal atomic bonding across the interface rather than metal-gas or metal-oxide bonding, which might exist under certain circumstances, e.g. the oxide is soluble in the bulk metal as in titanium. This assumption is based upon the fact that metal-oxide (or nitride) bonding would

be more ionic or covalent in nature, and consequently, more brittle while the metal-gas bonding, e.g. argon, would be of the very weak Van der Waal's type, which will tend only to interfere with the full strength of the metal-metal bonding.

Any study with the purpose of investigating the nature of adhesion under atmospheric conditions must contend with the problems of oxide or adsorption interference since the rate of a monolayer formation on a pure metallic surface under these conditions is much less than a microsecond. Two recent studies have approached this problem from different directions with similar results. Sikorski (12) has recently extended an excellent study of twist-compression bonding which was initiated by Anderson (13) and permitted the measure of a value for adhesion strength. These data are reported as the "median coefficient of adhesion". The median coefficient was defined as the ratio of the breaking force to the loading force averaged over several tests since experimental reproducibility was poor. In such a system a mechanical motion at the interface, which in effect seals itself from the air by displaced metal, is utilized to rupture the brittle oxide by yielding the ductile substrate. In so doing, the free metal atoms are exposed incidentally across the interface and a metal-metal bond is formed. Anderson (13) illustrated that the interface created in such an experiment will consist of a highly blended mixture of Surface I, Surface II, and oxides such that interpretation and/or reproducibility would be difficult. The results of this experiment will be discussed in the "Interfacial Atomic Bonding" section. It is interesting to note that if we down scale this experiment about 10^{+7} times we are in effect duplicating the plastic deformation-adhesion process experienced by the asperities expressed by Bowden's group as a portion of the frictional force equation.

Another significant contribution lies in the roll-bonding studies of McEwan and Milner (14) in which metal plates were brush cleaned, riveted together and rolled as a sandwich in a mill. The degree of bonding, i.e. bond strength, was measured as a patch shear tensile test utilizing opposite sides of the bonded sandwich as the tensile arms on either end of the patch. This was accomplished by cutting at different locations, i.e. about 1/2" apart in a 1/2" width, on opposite sides of the composite to a depth of the interface and measuring the tensile strength in shear of the remaining patch area. The results indicated at least 40% deformation was required to initiate adhesion in an aluminum-aluminum composite[*]. Seventy percent deformation was necessary to obtain the bulk strength of the aluminum. A number of dissimilar metal-pairs were tested and adhesion of one form or the other took place in all cases. The nature of this process suggests a slightly different deformation process;

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[*]Note in Proof: Communication with Milner's Group, Sept. 16,1963 indicates that only 2% deformation is necessary for aluminum-aluminum adhesion in a vacuum of 10^{-6} Torr.

however, the end result is quite similar to Sikorski's approach. That is, the substrate yields in the absence of atmospheric gases which ultimately allows metal atom-metal atom contact and interaction. Semenov (15) contended that mechanical cleaning and testing in an argon atmosphere changed the seizure mechanism significantly in that the percent of deformation necessary to permit seizure decreased from 80% to less than 10% as the temperature was increased from -200°C to 450°C. However, if we accept the fact that argon is weakly adsorbed on silver and the strength of the bond is a function of temperature, i.e. weakened by thermal vibrations, argon behaves much like any other gas in its interference in the proposed adhesion mechanism.

The possibility of mechanical adhesion must be mentioned in regards to relating experimental data to an ideal adhesion value since both of the above processes involve a very high force normal to the interface. There is a degree of probability that in the working process, twist-compression or roll-compression, the softer metal may be extruded into minute cracks in the surface of the harder material, or asperities might be forced into an interlocking position. Either of these effects will add strength to the adhesion joint in a mechanical sense; however, neither will be due to what we have called "chemical adhesion". If the chemical adhesion coefficients are to be measured, the mechanical contributions should be excluded from the final evaluation.

A third approach to this problem has recently been concluded in this laboratory (9) which involves the contact of two surfaces, which were treated to a condition of nearly ideal cleanliness in an apparatus as shown in Figure 1. The test samples consisting of a 1 cm square plate (A) and a spherically-tipped 2 mm rod (B) were mounted in an all glass ultra-high vacuum system of about one liter volume similar to that described recently by Redhead (16). The stationary plate was mounted on a nickel-tungsten through-seal allowing electrical continuity to the outside of the cell while the rod was mounted on a soft iron slug (D), which acted as a movable piston in a side arm of the glass system. The rod was attached so that electrical continuity to the outside was achieved through a spring and a through-seal. This configuration allowed the rod to be brought into touch contact with the plate by magnetic manipulation of the soft iron core. A tungsten filament (C) was also mounted near the rod-plate assembly in the system to act as an electron source for electron bombardment. The investigations were conducted by placing a clean pure metal plate and rod into position, evacuating to about 10^{-7} Torr and baking the entire system at about 450°C overnight. Upon completion of the bake-out cycle, the filaments were degassed by electrical flashing and the glass system was isolated by the
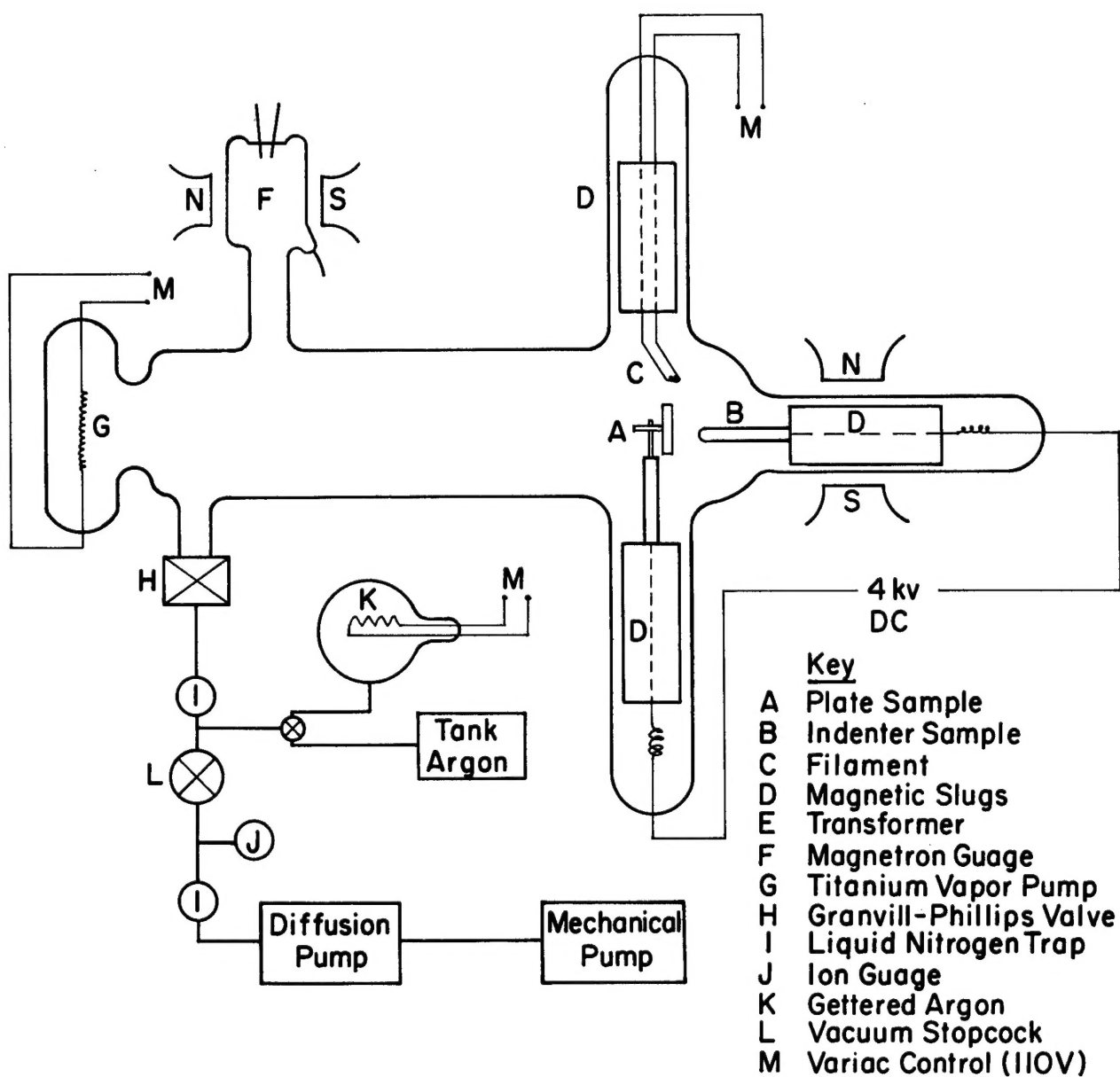
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Key

A   Plate Sample
B   Indenter Sample
C   Filament
D   Magnetic Slugs
E   Transformer
F   Magnetron Guage
G   Titanium Vapor Pump
H   Granvill-Phillips Valve
I   Liquid Nitrogen Trap
J   Ion Guage
K   Gettered Argon
L   Vacuum Stopcock
M   Variac Control (IIOV)

FIGURE I: Adhesion Apparatus

use of a Granville-Phillips valve (H). The vapor-titanium sorption pumps (G) were flashed and within an hour or so the pressure within the system was reduced to the 10^{-11} Torr range as measured by a Redhead Magnetron Gauge (F) (NRC-552). At this point high purity argon was admitted to the system to a pressure of about 10^{-3} Torr and the specimen surfaces were cleaned by argon ion bombardment alternately for a period of about 15 minutes per side. The sputtered metal residue from the surfaces insured a low partial pressure of the chemisorbed gases within the system. The system was then re-evacuated to allow electron bombardment of the surfaces to remove the physically adsorbed argon. At a final pressure of about 5×10^{-11} Torr the surfaces were brought into touch contact, i.e. with a minimum of force. The purpose of the nearly forceless contact was to reduce the mechanical working of the interface to a minimum. The reduction of the mechanical working component to zero is highly improbable as illustrated in the aforegoing discussion of the surface asperities. Adhesion was observed as the force required to withdraw the rod and careful micrographic inspection of the contact area after the parts were removed from the apparatus. A discussion of these results will follow in the next section.

A simple experiment was conducted in the apparatus just described which illustrates the significance of an adsorbed inert gas layer and its effect on adhesion. A nickel plate was mounted in a horizontal position and a side arm constructed to contain liquid gallium. The apparatus was subjected to the normal bake-out cycle and nickel surface cleaning as described, except that the electron bombardment desorption step was omitted. A drop of gallium was then permitted to fall on this nickel surface. The gallium did not wet the nickel; however, when the cycle was repeated and the electron bombardment desorption step included, wetting was immediate and complete. Gallium would not wet nickel under atmospheric conditions unless the oxide layer was ruptured. These results should not be too surprising if one considers that the heat of adsorption of the inert gases on tungsten and other transition metals is in the order of 2 - 10 Kcal per mole (17). These adsorbed inert gases will interfere with forceless metal-metal contact, although not as energetically as that which might be expected by chemisorbed molecules of oxygen, nitrogen, etc. The adhesion results of a liquid on a solid should establish the ultimate in bonding conditions at the interface since the liquid will conform identically to the solids surface without the use of mechanical action, and the high atomic mobility in the liquid will permit the lowest energy sites in the interface to be occupied, i.e. maximum interfacial bond strength.

Interfacial Atomic Bonding

As a final consideration in the analysis of an ideal adhesion, let us

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consider the atomic forces across the interface under the ideal conditions set forth in the definition and in particular the state of affairs existing when the two metals involved in adhesion are the same, e.g. aluminum-aluminum or platinum-platinum. According to the discussion above, all such pairs ought to yield macro-bond strengths similar to their bulk strength in an ideal adhesion with strength decreases due to interference at the interface caused by gas adsorption and/or crystallographic misorientation. In adhesion testing in high vacuums (1 atmos. -10^{-7} atmos.) where gas readsorption can take place in a matter of milli-seconds or less, and intimate metal-metal contacts rely upon a mechanical dis-ruption of the existing surface oxide, one would expect the amount of intimate metal contact to be a function of oxide character, hardness of the metal substrate and to some degree the nature of the atomic bonding involved in the metals under investigation. The hardness of the metal substrate is important from the stand-point that if the substrate is soft, as in indium, small forces are required to cause a rupturing of the oxide surface layer which is relatively brittle; and further, the soft substrate will also allow a sealing of the contact zone from the atmospheric gases which could readily diffuse into the barred metal region and readsorb on the exposed reactive metal. The gases adsorbed on the oxide are capable of surface diffusion and will also play a significant role. The metals such as gold, platinum and palladium, which form relatively unstable oxides under normal conditions, are not plagued with massive crystalline oxide de-posits which interfere with adhesion. Physically adsorbed gases will, however, play a part. For example, platinum will not weld to platinum under atmos-pheric conditions; but, will weld completely on contact after the parts are heated in a vacuum of 10^{-6} Torr. This is not possible with the other transition metals which form stable oxides.

If the mechanical process involved in the adhesion is capable of in-creasing the localized temperatures of certain areas near or to the melting point as suggested by Bowden (3), two effects may result. Such an occurrence would allow surface or interfacial diffusion to occur, which in turn would allow a more intimate approach of the two surfaces than would be experienced in a single contact experiment. A second effect involves the relation between the metal and oxide. Since titanium and a number of other metals are capable of dissolving significant quantities of oxygen, nitrogen, etc. into their metal lattices, this would provide a second mechanism of surface impurity removal which would suggest that the amount of adhesion would increase with tempera-ture above the diffusional range. Since localized high temperatures are possi-ble in mechanical tests mentioned in the previous section, it is not surprising that Sikorski's mean coefficient of adhesion data corresponds quite favorably to a plot against the metal melting point as shown in Figure 2. The three
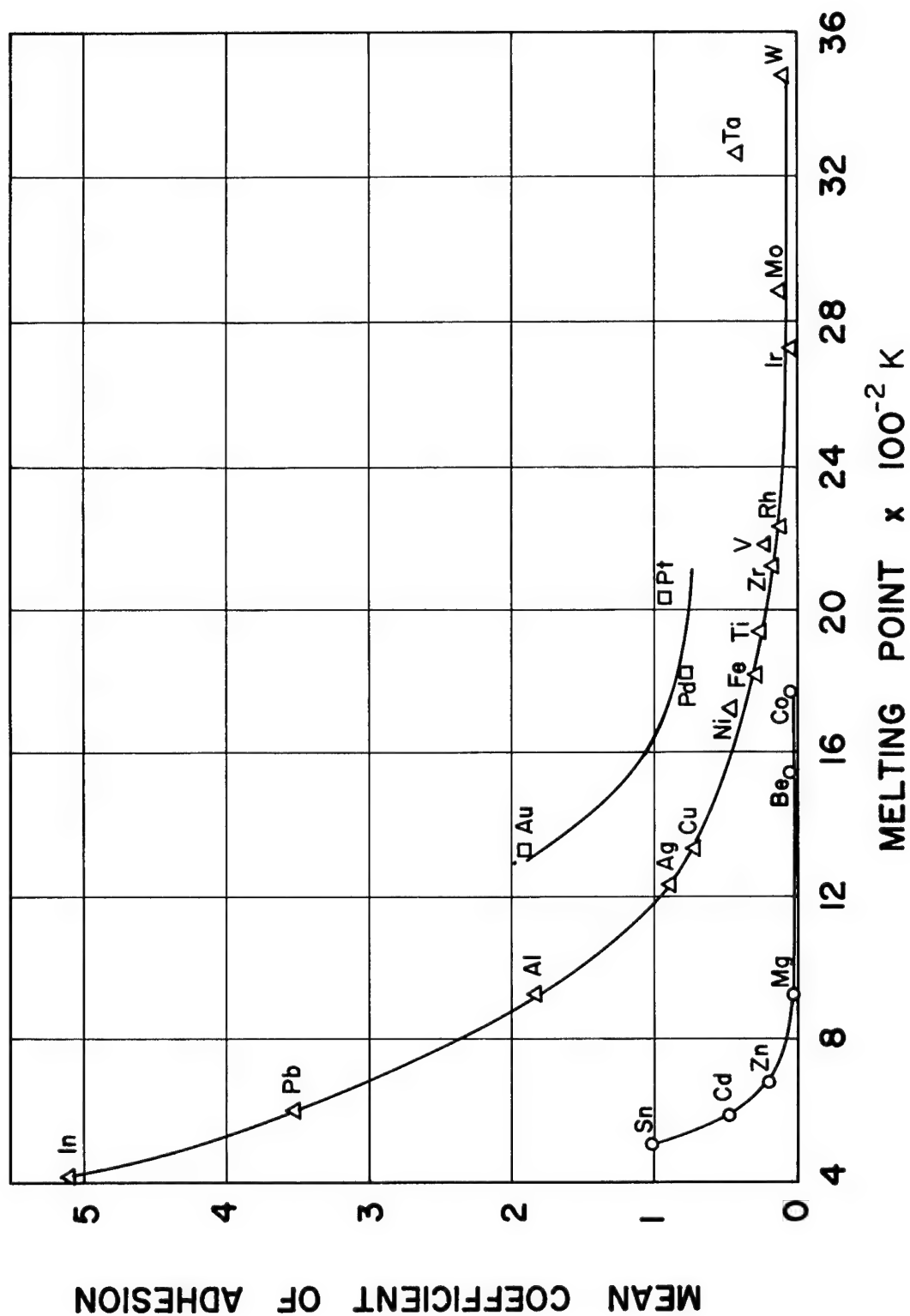
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FIGURE 2: Mean Coefficient of Adhesion * versus Metal Melting Point

*Sikorski (12)

separate curves seem to suggest three different mechanisms; however, if we consider that gold (Au), platinum (Pt), and palladium (Pd) do not form stable oxides, we would expect to find a higher degree of adhesion than in corresponding transition metals, nickel (Ni) and copper (Cu), even though the crystal structures are identical in all cases. The central curve appears to represent the behavior of normal metals, the adhesion coefficient increases with increasing ductility and decreases with melting point. The third curve, however, presents an interesting case, the mean coefficient of adhesion is about 80% lower than the other metals. The metals representing this curve with increasing melting point are tin (Sn), cadmium (Cd), zinc (Zn), magnesium (Mg), beryllium (Be) and cobalt (Co). The metals in the list all form stable oxides and, in general, apparently respond to the ductility-melting point up-swing as indicated in the central curve. The crystal structure of Cd, Zn, Mg, Be, β Co is hexagonal while tin is body-centered tetragonal and α Co is face-centered cubic. A relationship seems to exist if one compares the unit cell ratio of c/a of the hexagonal metals with the respective position on the curve as shown in Table 1.

TABLE 1

c/a (18)	Mean Adhesion Coefficient (12)
Cd - 1.8856	0.45
Zn - 1.8563	0.20
Mg - 1.6235	0
Be - 1.5677	0
β Co - 1.6232	0

Although these data appear to provide a relationship, an analysis of the structures, according to Hume-Rothery (8), seems to provide an explanation as to why these particular metals have such a low coefficient of adhesion. White tin with an atomic nearest neighbor coordination number of four (two next nearest neighbors), and hexagonal cadmium and zinc with six nearest neighbors in the close packed plane, and six next nearest neighbors in the adjacent planes, adhere to the (8-N) bonding rule which is usually applied to the more covalent compounds. A molecular orbital bonding approach to the transition metals suggested by Trost (19) concluded that the major contribution to cohesion in Group IIb hexagonal metals should be from an (sp^2) intralayer hybridization band and a (p_z) bonding band interlayer, which results in a slightly higher degree of bond directionality than would be expected in the cubic transition metals. This agrees with the slip planes for these metals which may justly infer a degree more of covalency than is found in the other transition metals. Beryllium, magnesium, and β cobalt have not been considered in this respect; however, due to a c/a ratio less than ideal (1.633), one would expect a less

exaggerated effect than is found in cadmium. α cobalt is face centered cubic and related very closely to nickel in its chemical behavior and physical proper-ties; however, there exists a slight difference ($\Delta = 0.2$) in the respective mean adhesion coefficient which is not readily explained.

It should be evident from the discussion thus far that an attempt to reduce the ideal adhesion strength to a mathematical equation would involve so many unknowns that an evaluation would be hopeless. For example, the true area of contact, although dependent upon the normal bulk mechanical properties, must also be a function of the brittleness, diffusibility and adhesive properties of the oxide of the metal since it is not the amount of oxide moved at the interface but the amount of metal atom-metal atom contact, which will be important. Apparently, no reliable techniques have yet been established to estimate this value as discussed by Sharpe in a recent symposium arranged by the Institute of Physics at Belgrave Square (20).

Ideal adhesion between unlike metals (A and B) must be non-equilibrium with respect to the bulk phases since the electrochemical potential ($\bar{\mu}$) of species A in phase B is not equal to that of A in A which is the criteria for thermo-dynamic equilibrium in a system (21). The equilibration of $\bar{\mu}$ may only take place if the temperature is raised which in turn changes the problem. The degree of diffusion across or within the interface, which may be permitted without changing the problem, is another matter of contention. For example, let us place in ideal adhesion two one-centimeter rods, one of gold and the other of silver, which form a continuous series of solid solutions if allowed to come to equilibrium. Then let us raise the temperature and allow diffusion to take place so that an alloy is formed over a distance of about one centimeter. Our original problem has now reduced to two interfaces, pure gold-alloy and pure silver-alloy. The formation of intermetallic compounds and diffusion voids, as illustrated by ex-perimental results of the Kirkendall effect, may render the phenomena of pure adhesion uninterpretable. In order to avoid these complications let us confine conditions to those which will permit only a small degree of surface diffusion to take place and negligible bulk diffusion. Thus the interface is limited to several unit cells in thickness and the electrochemical potentials of the com-ponents are not equilibrated throughout the system. The purpose of initiating a discussion involving the thermodynamic equilibrium lies in the necessity to re-ly upon thermodynamic principles to evaluate the probability of an atomic bond formation across the interface. Since equilibrium is not established, a question may be raised against these thermodynamic arguments and this should be realized immediately.

Early in this century Harkins (22) developed an equation which related to the surface and interfacial energies in an adhesion of a liquid to a solid.

According to this relationship, the work of adhesion is equal to the sum of the two surface energies less the interfacial energy after adhesion. As mentioned in the gallium-nickel experiment, interfacial equilibrium is approached when a mobile liquid is placed upon a surface; however, when both surfaces are solid interfacial equilibrium and orientation effects would be expected to complicate the picture. For example, using the presumption that equilibrium energy values are necessary for the estimation of the work of adhesion by Harkins' equation, let us consider the case of the gold and silver rods in ideal adhesion mentioned above. The interfacial energy, if equilibrium conditions are imposed, is essentially non-existent since equilibrium is only achieved when the electrochemical potentials in each phase are identical, and according to the equilibrium diagram this will only occur in complete solid solution. Restricting interfacial energy to a real case by approximation still does not solve the problem since solid surface energy values are still a matter of conjecture and may be an order of magnitude too small as suggested by J.O.H. Varley (20). Atomic and planer orientation effects in metals would be extremely difficult to analyze. The analytical aspects of these shortcomings have been discussed by Eley (23).

A second approach to the analysis is in the consideration of the behavior of a number of metal A atoms in an atmosphere of B atoms under conditions where equilibrium is readily achieved. If the metal A atoms tend to prefer B atoms as neighbors, a solid solution or intermediate phase may be formed. On the other hand, if A atoms prefer A atoms as neighbors in preference to B atoms, an immiscible mixture is formed. Temperature versus composition equilibrium diagrams present these data for nearly all metal pairs and the equilibrium thermodynamics differentiating the two processes have been discussed in a number of texts (21, 24).

If an atomic bond is to be formed across the interface during ideal adhesion a negative free energy of atomic bond (A-B) formation must exist, which is indicated in the thermodynamics leading to the free energy-composition diagrams discussed by Darken and Gurry (24). This formation energy is enhanced by the loss of free surface energy of the two surfaces during the adhesion, but is reduced by crystallographic misalignment in coordination with the ability of A and B to form nondirectional bonding. It is improbable that the unit cell size of A is identical with that of B such that atomic coincidence is now impossible over great distances; thus the ability to form partial bonds, i.e. distorted bond angles and distances, would increase the interfacial bond strength.

If the atoms A and B are such that they form an intermetallic compound which has a very negative free energy of formation and the interfacial conditions are such that this compound is allowed to form, i.e. heating to diffusional range, a loss in bulk adhesive strength might be expected as a consequence of the observed properties of the intermetallic compound itself. Most pure

polycrystalline intermetallic compounds are quite brittle as cited in the case of nickel-aluminide. McEwan and Milner observed a complete loss in bulk strength when they subjected well-bonded metal couples to a post heat-treating cycle when the components formed a strong intermediate phase. Structural voids observed in Kirdendall diffusion experiments may also contribute to this interfacial weakness.

In this interpretation of adhesion bonding the readers might have noted the similarity to gain boundary strength: a case of adhesion in which both phases are in thermodynamic equilibrium. Solid solution grain boundary strength is high compared to that of the intermetallic compounds. It seems probable that this might be interpreted further, on the basis of ionic or covalent bonding in these compounds, or of a loss in metallic character in the atomic bonds of the compounds. The electrical properties of a number of intermetallic compounds are in support of this view.

Certain combinations of metal couples $\underline{A}$ - $\underline{B}$ have a positive free energy of atomic bond formation, that is, work must be done on the system to create an atomic mixture. Equilibrium diagrams of such systems involve a large degree of immiscibility, e.g. copper-molybdenum or silver-nickel, which extends to room temperature. Care in interpretation must be taken for a number of metal pairs, such as iron-tin, are immiscible in the liquid state yet form a number of compounds in the solid state. Providing the positive free energy of bond formation is not exceeded by the loss in surface free energy experienced by the components during adhesion, no interfacial bond should form. For example, one would expect ideal adhesion to exist between an atom, or even a monolayer, of silver atoms on a pure surface of iron; however, if the silver phase is a centimeter thick there is a preference of the interfacial silver atom to remain with the silver phase rather than with the iron phase. An interfacial force probably exists; however, one would expect its magnitude to be far below the cohesive forces of either bulk phase.

The ultimate objective of the ultra high vacuum apparatus used to clean the plate and rod completely for adhesion studies discussed above, was to examine the interpretation just cited. The results are shown in Table 2.

TABLE 2

Adhesion Observed	No Adhesion Observed
Iron-Aluminum	Copper-Molybdenum
Copper-Silver	Silver-Molybdenum
Nickel-Copper	Silver-Iron
Nickel-Molybdenum	Silver-Nickel

The metals in the "Adhesion Observed" column all form some form of inter-mediate phase denoting a negative free energy of atomic bond formation while those in the other column are all immiscible suggesting a positive free energy of bond formation.

The suggestion that immiscibility of one metal with another as a criteria for seizure resistance was presented as the results of a boundary lubri-cated sliding study of various elements on steel, aluminum, copper and silver by Roach, Goodzeit and Hunnicutt in 1956 (25) and discussed by Goodzeit in 1959 (26). The elements immiscible with the base metals provided good or fair resistance to seizure even with kerosene lubrication. The observed exceptions were lithium, magnesium, calcium, barium on steel, carbon on aluminum, carbon and iron on copper, and carbon, molybdenum and nickel on silver. Also of interest is their observation that a number of highly covalent semimetals, e.g. germanium, antimony, selenium, and tellurium, generally show a good to fair resistance to seizure against the base metals.

Conclusions

The phenomena of metallic adhesion on an atomic scale appears to be intimately involved in the processes of friction, cold welding, powder com-pacting, grain boundary strength and fatigue. Each of these processes intro-duce a number of variables which are difficult, if not impossible, to control, and as such tend to complicate the study of the fundamental phenomena. Probably the most necessary conditions for a successful metallic adhesion experiment involve the forceless interaction of two atomically clean surfaces at a tempera-ture below the bulk diffusion range which to this date has not been successfully achieved. An analysis of the interatomic forces involved in the adhesion energy solution will be even more complex than those involved in simple solid surface energy problems, which are still unresolved in a mathematical sense. The im-mediate problems in a qualitative solution appear to be the establishment of a standard experiment meeting the requirements discussed above within practical limitations, a precise technique to estimate the area of metal-metal contact, which in all of the above studies is unknown and a method to resolve the inter-facial crystal structure. Until these problems are solved with a degree of accu-racy, values of bulk interfacial strengths will have little meaning in relation to the true nature of metallic adhesion.

Acknowledgements

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<div align="center">APPENDIX I</div>

EXPERIMENTAL

Phase I: Effect of Temperature and Contact Area On Adhesion

Little is understood of the contact area involved when two surfaces are brought together as indicated in the previous section. Without this information interfacial strength values are of little consequence. A further question may be proposed as to the effect of temperature on the junction and its strength. Since these problems are intimately tied together, an apparatus was designed, as shown in Figure Al, which will be capable of measuring the various electrical parameters of two atomically clean surfaces pressed together with a known force at a specific temperature. It is anticipated that these data may provide reproducible force versus resistance data which can be related to contact area values. An absolute resistance measuring device which will eliminate contact potential effects has been constructed and standardized for use in these experiments. The cell apparatus shown in Figure Al will be manipulated similarly to that discussed in the previous section. When the surfaces are clean the 1 rpm motor (H) will drive the micrometer screw (G) such that the indentor (A) will advance at a rate of about 0.01 mm/min. to a point of contact. From this point the strain as measured in the strain gauge (C) will be compared to the observed resistance of the junction. Potential measurements may also be included in this series.

Phase II: Surface Energy of Silver

As indicated in the previous section reliable surface energy data for metals at temperatures well below their melting point is quite unreliable. As a consequence, adhesion energies values will be unattainable. An approach to the determination of these values was initiated during the 1962 period and a description set forth in the final report of that period[*].

In reference to the various sub-units, i.e. liquid gas calorimeter, power metering equipment and BET apparatus; all units were tested independently; and standardized. However, as a combined unit the initial design of the low vacuum seals in the calorimeter section did not allow a positive seal at cryogenic temperatures which permitted an excessive heat leak in the system. A minor design modification which is currently in progress is expected to rectify this problem. Experimental results are expected within a short period.

Phase III: Interfacial Structure in Metallic Adhesion Systems

The discussion of interfacial structure as cited in the previous section outlines the principal problems facing an investigator. Of particular interest is the definition of the interface with respect to the amount of bulk diffusion

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[*] Keller, D.V., "Adhesion Between Atomically Clean Metallic Surfaces" Semi-Annual Report, N62-13821; Final Report, N62-15678, 1962.

Key

A Samples
B Insulator
C Pressure Sensor
D Bellows, Stainless Steel
E Glass-Metal Seal
F Aluminum Support
G Micrometer Movement
H I rpm Micrometer Drive
I Tungsten Filaments & Shield
J Temperature Bath
K Copper-Constantan Thermocouples
   and Resistivity Leads
L Strain Guage
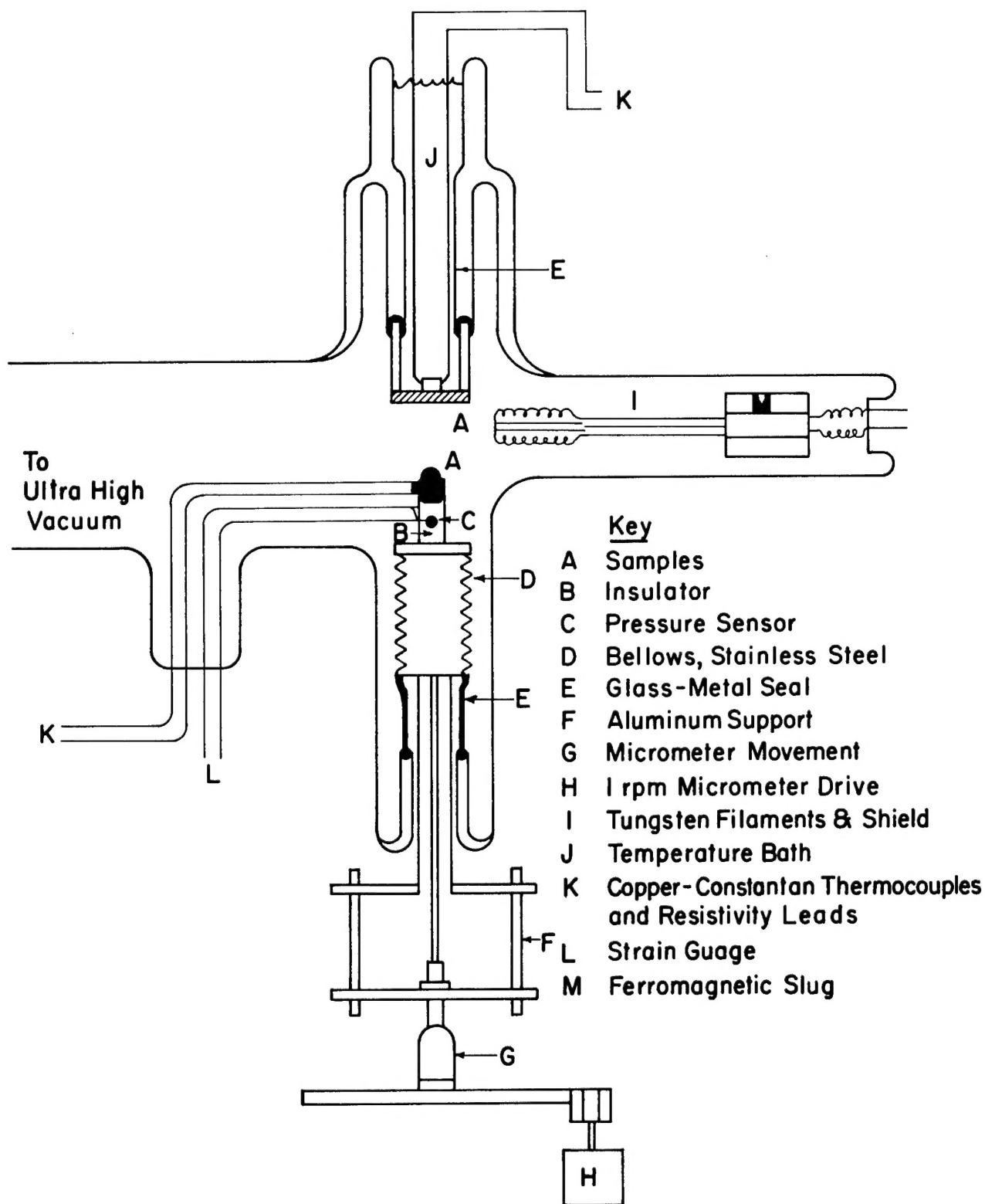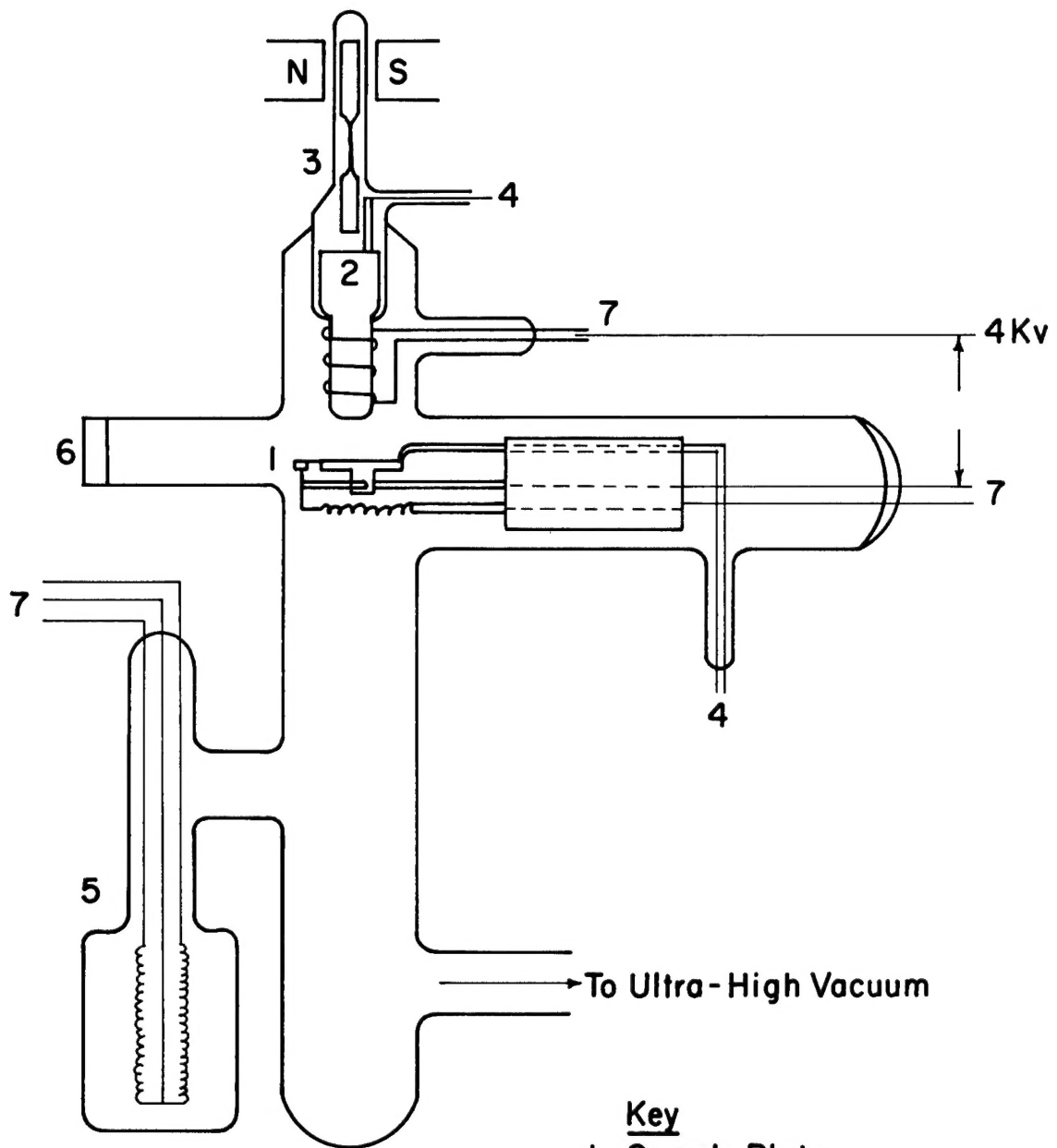M Ferromagnetic Slug

To Ultra High Vacuum

FIGURE AI: Vacuum Cell

which can take place without drastically changing the problem. Thus, by definition the adhesion interface between two different metals must be in a state of non-equilibrium and only a few atomic layers thick. If this is the case it is unlikely that this narrow region bathed in low voltage electrons will provide sufficient diffraction intensity to allow an analysis. There is little doubt that a sorbed layer, or possibly several layers, of metal atoms on a metal substrate could be described; however, indications cited in the previous section are that these data will have little relation to the case in which a bulk metal is in contact with a second. As a consequence, this approach was temporarily shelved in lieu of a more important study.

There appears to be some conflict of results when our data is compared to that obtained from the roll-bonding studies by McEwan and Milner as cited in the previous section in regards to the adhesion of immiscible pairs. For example, they observed a mechanically stable bond when plates of copper and molybdenum were rolled as a sandwich to high degrees of deformation. The question arises as to whether or not the bond they observed was due to a mechanical or chemical mechanism. In pursuing this question further another study is under way at Syracuse to determine the contact angles between a liquid metal resting on an atomically clean metal plate for cases in which the two metals are immiscible. Since the metal atoms in the liquid state are extremely mobile and will readily achieve the lowest energy sites on a surface, ideal conditions for an interfacial bond will be present without an effective mechanical force. The apparatus being constructed for this study is shown in Figure A2 and will be operated in a manner similar to that described previously.

Liquid metal held in container (2) by surface tension and heated by filament (7) is forced on to an atomically clean plate (1) by magnetically moving a plunger (3) into the container. A drop will fall on to the plate to be observed and photographed for contact angle measurements.

It is anticipated that these data may establish the immiscibility criteria cited for non-adhesion and may also provide information on the behavior of liquid metal lubricants for space applications.

Key
1 Sample Plate
2 Liquid Metal Container
3 Plunger
4 Thermocouples
5 Titanium Sorption Pump
6 Observation
7 Power Lead

FIGURE-A2: Contact Angle Measurements in Ultra High Vacuum.

NASA TN D-2228
National Aeronautics and Space Administration.
ADHESION BETWEEN ATOMICALLY CLEAN SUR-
FACES. Douglas V. Keller, Jr., Syracuse University
Research Institute. February 1964. i, 22p. OTS
price, $0.75. (NASA TECHNICAL NOTE D-2228)

A broad definition of adhesion between solid metals
is proposed and discussed in order to permit a better
understanding of the vast amount of metallic adhesion
data being published currently. An interesting result
of the definition in this paper is that there appears to
be a real relationship between adhesion phenomena
and the processes of friction, cold welding, sintering,
grain boundaries strength and fatigue. A number of
experimental techniques are discussed and analyzed
with respect to increasing our knowledge of adhesion
phenomena.

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   Jr.
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III. NASA TN D-2228

NASA

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